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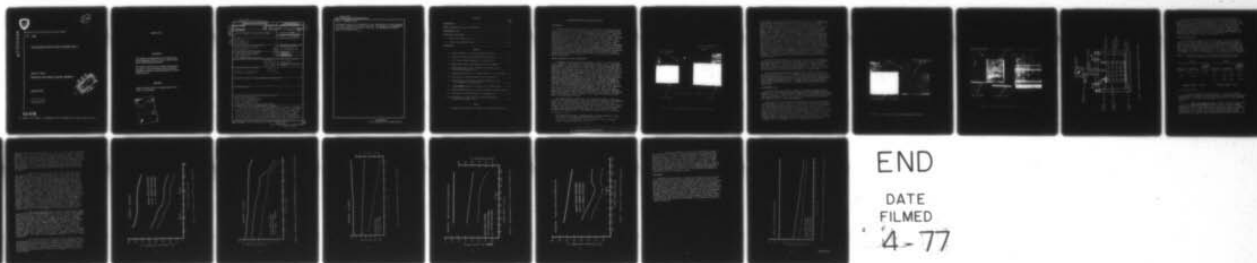
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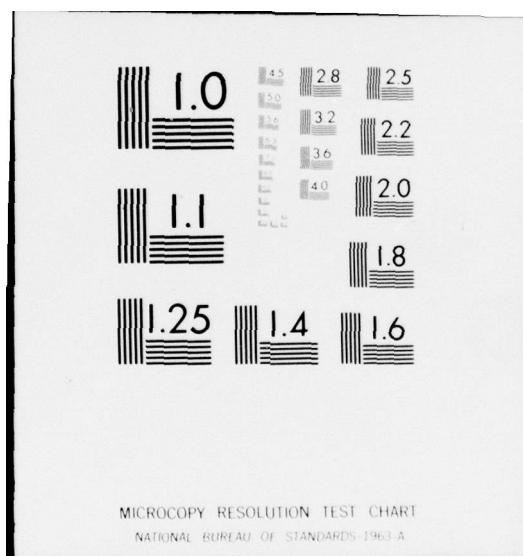
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Research and Development Technical Report

ECOM - 4465

## RECHARGEABLE METAL OXIDE-HYDROGEN CELLS

James E. Wynn

Electronics Technology & Devices Laboratory

January 1977

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Item 20. ABSTRACT (Cont)

rechargeable cells have been measured at room temperature at current densities up to 100 milliamperes per square centimeter. The Faradaic and thermodynamic efficiencies and cycle life of the cells have been determined at various charge and discharge rates.



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## CONTENTS

	<u>Page</u>
INTRODUCTION . . . . .	1
ANODE PREPARATION AND CELL CONSTRUCTION. . . . .	1
EXPERIMENTAL PLAN . . . . .	3
RESULTS AND DISCUSSION . . . . .	7
1. Nickel Oxide-Hydrogen Cells. . . . .	7
2. Silver Oxide-Hydrogen Cells. . . . .	10
CONCLUSIONS . . . . .	16

## FIGURES

1. Basic Components of Nickel Oxide-Hydrogen Cell. . . . .	2
2. In-House Fabricated Platinum-Hydrogen Electrode . . . . .	4
3. Cell Pack and Basic Components for AgO/H <sub>2</sub> Cell. . . . .	5
4. Experimental Metal Oxide-Hydrogen Test Cell Chamber . . . . .	6
5. Charge/Discharge Curves of Nickel Oxide-Hydrogen and Silver Oxide-Hydrogen Cells . . . . .	8
6. Voltage Characteristics vs Current Density for NiO/H <sub>2</sub> Cells . . . . .	9
7. Efficiencies vs Current Density for NiO/H <sub>2</sub> Cells. . . . .	11
8. Efficiencies vs Cycle Life at Current Densities from ~ 20-25 mA/cm <sup>2</sup> for NiO/H <sub>2</sub> Cells . . . . .	12
9. Voltage Characteristics vs Cycle Life for NiO/H <sub>2</sub> Cells . . . . .	13
10. Voltage Characteristics vs Current Density for AgO/H <sub>2</sub> Cells . . . . .	14
11. Efficiencies vs Current Density for AgO/H <sub>2</sub> Cells. . . . .	15
12. Efficiencies vs Cycle Life at a Current Density of 50 mA/cm <sup>2</sup> for AgO/H <sub>2</sub> Cells . . . . .	17

## TABLE

1. Voltage-Time Plateaus for Charging NiO/H <sub>2</sub> and AgO/H <sub>2</sub> Cells. . . . .	7
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## RECHARGEABLE METAL OXIDE-HYDROGEN CELLS

### INTRODUCTION

Several independent studies have been conducted and engineering design models constructed of nickel oxide-hydrogen and silver oxide-hydrogen cells as possible power sources for orbiting satellite applications.<sup>1,2</sup> The cells are reported to have a long cycle life capability and can be overcharged repeatedly without serious damage to cell operation and efficiency. Although cell voltage reversal can occur on discharge, the voltage reversal has no appreciable effect on cell efficiency and cycle life, especially in nickel oxide-hydrogen cells. However, silver oxide-hydrogen cells have a more limited cycle life capability due to silver migration through the separators, resulting in subsequent shorting. This study examines in detail the current-voltage characteristics for charging and discharging nickel oxide and silver oxide-hydrogen cells and presents the Faradaic and thermodynamic efficiencies of the cells for charging and discharging up to the 2C rate (100 mA/cm<sup>2</sup>). Charge and discharge efficiencies as a function of cycle life of the cells are also discussed.

### ANODE PREPARATION AND CELL CONSTRUCTION

A standard sintered nickel-oxide cathode, 5.08 cm x 3.8 cm x 0.102 cm, shown in Figure 1, was used in the nickel oxide-hydrogen cells. The cathode had a capacity of approximately 1.0 ampere-hours. This electrode was pre-charged for 15 hours at 0.4 A in 30% KOH electrolyte against a nickel counter electrode. The charged nickel-oxide cathode was placed in a folded layer of potassium titanate paper - the dimensions being 10.8 cm x 6.99 cm x 0.0254 cm. Two folded layers of polyamide Pellon 2506K, each being 10.8 cm x 6.99 cm x 0.127 cm, were then placed on top of the KT layer. The KT layer of the dual separator configuration served as an electrolyte reservoir, while the Pellon layer functioned as an electrolyte absorbent wick. The Pellon separator also provides rapid KOH electrolyte absorption at high rates of charge and discharge without a significant decrease in the electrical conductivity of the cells. Two platinum/Teflon bonded hydrogen anodes, each being 5.08 cm x 6.35 cm x 0.033 cm and containing approximately 10 mg Pt/cm<sup>2</sup>, were placed on each side of the nickel-oxide cathode/separator pack. The single cell pack consisted of one nickel-oxide cathode sandwiched between two hydrogen anodes, the separator wrap consisting of one layer of KT paper on the cathode side, followed by two layers of Pellon 2506K. The platinum/Teflon bonded anodes were fabricated in-house.

The platinum powder (black) was first prepared chemically from chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) using sodium borohydride ( $\text{NaBH}_4$ ) as the reducing agent. The platinum black was washed with distilled water until free of sodium chloride and boride salts. The material was then vacuum dried in air to remove adsorbed and occluded hydrogen. This procedure minimizes the heat evolved by the hydrogen-oxygen redox reaction. Excess heat will promote sintering and crystal growth of the platinum black which results in a loss

- <sup>1</sup> M. Klein and M. George, "Nickel-Hydrogen Secondary Batteries," Proc. 26th Power Sources Symposium, May 1974, pp. 18-20.
- <sup>2</sup> L. E. Miller, "Metal-Hydrogen Battery Designs," Proc. 26th Power Sources Symposium, May 1974, pp. 21-24.



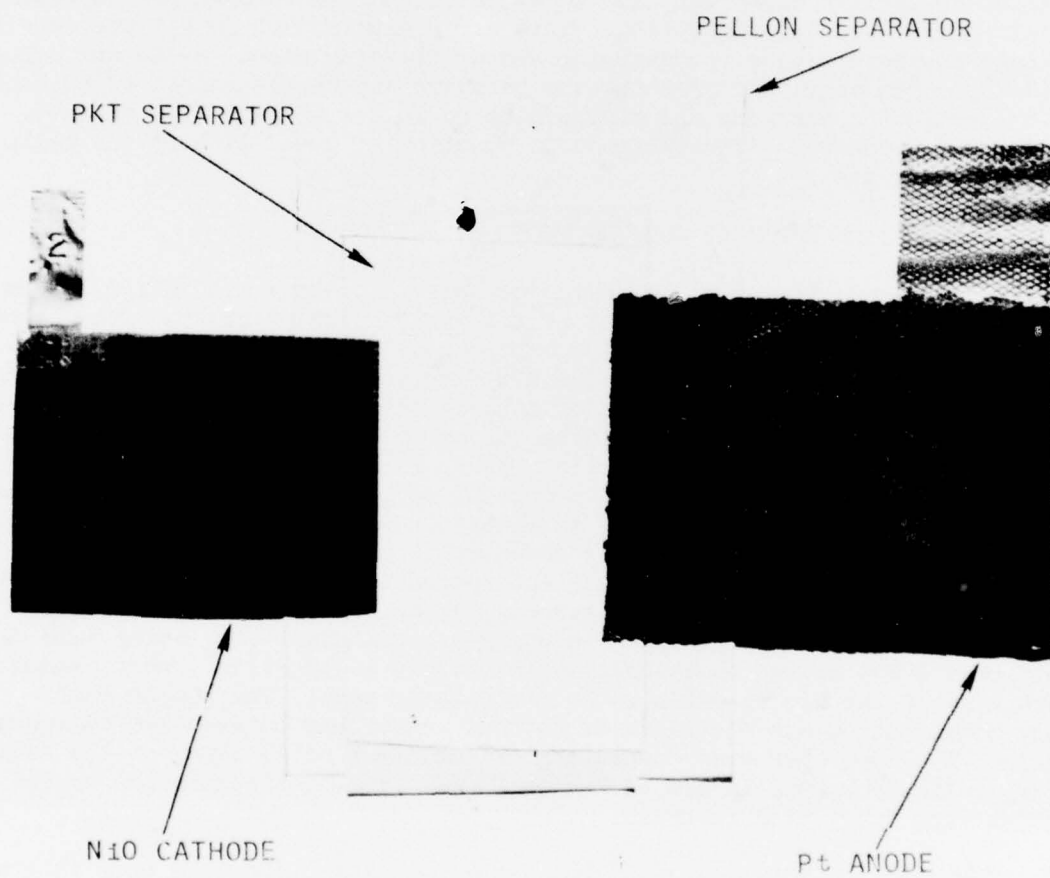


Figure 1. Basic Components of Nickel Oxide-Hydrogen Cell

in catalytic activity of the platinum particles. The two platinum/Teflon bonded anodes were prepared as follows: (a) a mixture of 1.5 grams of the platinum black was wetted with 1 cc of distilled water and 20 drops (0.05 cc/drop) of a solution of Teflon 41 BX emulsion containing 13 milligrams of Teflon emulsion per drop (resulting in a dry mixture of approximately 15% by weight of Teflon bonding agent), (b) the wet mixture was kneaded with a spatula to obtain a uniform blend of platinum and Teflon emulsion, (c) to this mixture 20 cc of acetone (C.P. Grade) were added and said mixture further kneaded until a uniform coagulated ball of platinum/Teflon was formed in the acetone liquor, (d) the acetone was decanted and fresh acetone was added several times to remove the emulsifying agents of the Teflon 41 BX mixture, (e) the coagulated platinum/Teflon mixture was rolled evenly with glass rods onto two expanded silver current collectors, each being 5.08 cm x 6.35 cm x 0.0254 cm, and (f) the resulting electrodes were air dried overnight. After drying, the electrodes were hot pressed at 200°C on to single layers of Chemplast fibrous porous TFE Teflon (5 mils thick) at a pressure of 246.08 kg/cm<sup>2</sup> for three minutes. The hydrogen anodes in their final configuration averaged about 0.033 centimeters in thickness. A platinum-hydrogen electrode prepared by the above method is shown in Figure 2.

The silver-oxide cathodes (2.86 cm x 4.13 cm x 0.033 cm) consisted of sintered silver powder pressed onto expanded silver screens. The cathodes were taken from zinc-silver oxide cells manufactured by Eagle-Picher Industries (Figure 3). A silver current collector (6.35 cm x 0.396 cm x 0.013 cm) was spot welded onto a coined corner of the electrode. The electrical capacity of the cathode was approximately 1.5 ampere-hours.

The silver-oxide cathodes were precharged at 375 mA for 15 hours in 30% KOH electrolyte prior to cell assembly. The separator system for the silver-oxide hydrogen cell consisted of two layers of fibrous sausage casing and cellophane sandwiched between two layers of Pellon 2506K. The separator clad silver-oxide cathode was then situated between two platinum/Teflon bonded anodes as shown in Figure 3. A complete cell pack is also shown in this figure.

#### EXPERIMENTAL PLAN

The test cells were cycled by means of an automatic charge/discharge apparatus which had a maximum current capability of 2.2 amperes. The timers could be set up to 24 hours either on charge or discharge. The current during charge and discharge was held constant by the instrument and was occasionally checked by means of calibrated ammeters.

The test cell for the nickel oxide-hydrogen and silver oxide-hydrogen electrode packs is shown in Figure 4. The test cell consisted of a stainless steel pressure chamber and cover with a wall thickness of approximately 1.27 centimeters thick. Attached to the cover was a pressure gauge (0 to 7.03 kg/cm<sup>2</sup>) and stop-cock valve arrangement for releasing or feeding hydrogen gas to the closed system. During the charging phases of both the nickel oxide and silver oxide-hydrogen cells, hydrogen was fed into the system at about 0.35 kg/cm<sup>2</sup> (5 psi). This was done because the low rate of hydrogen leakage at the sealed joints of the pressure vessel was sufficient to impair the cell performance of the low capacity electrode packs.

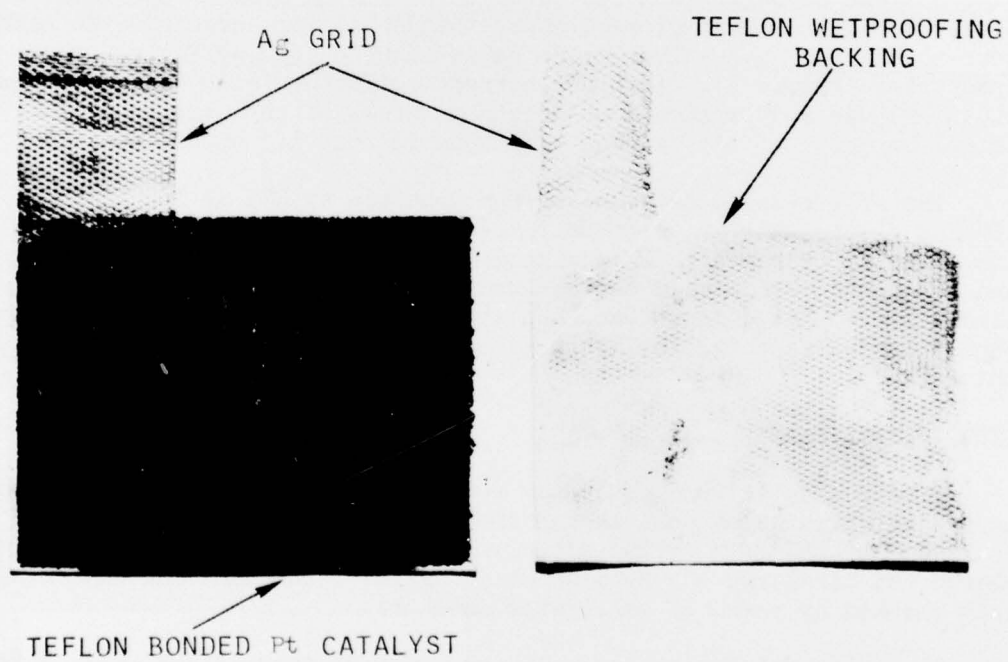


Figure 2. In-House Fabricated Platinum-Hydrogen Electrode

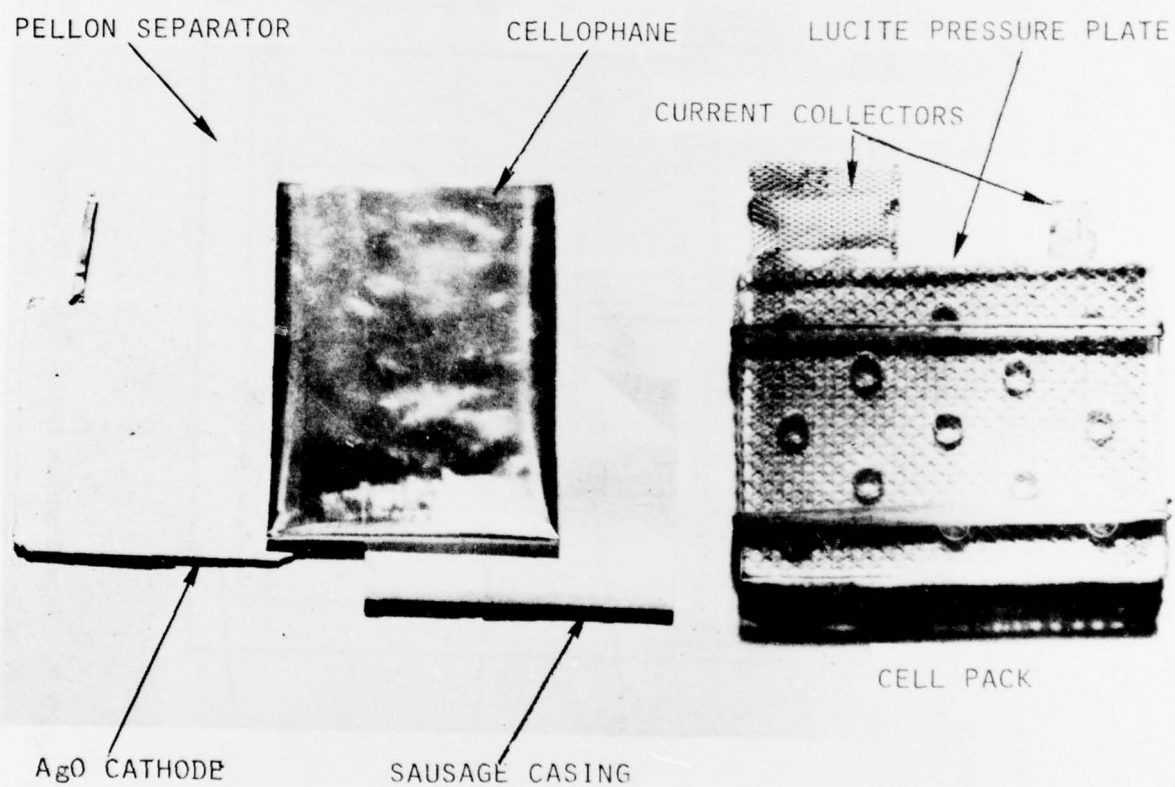


Figure 3. Cell Pack and Basic Components for  $\text{AgO}/\text{H}_2$  Cell

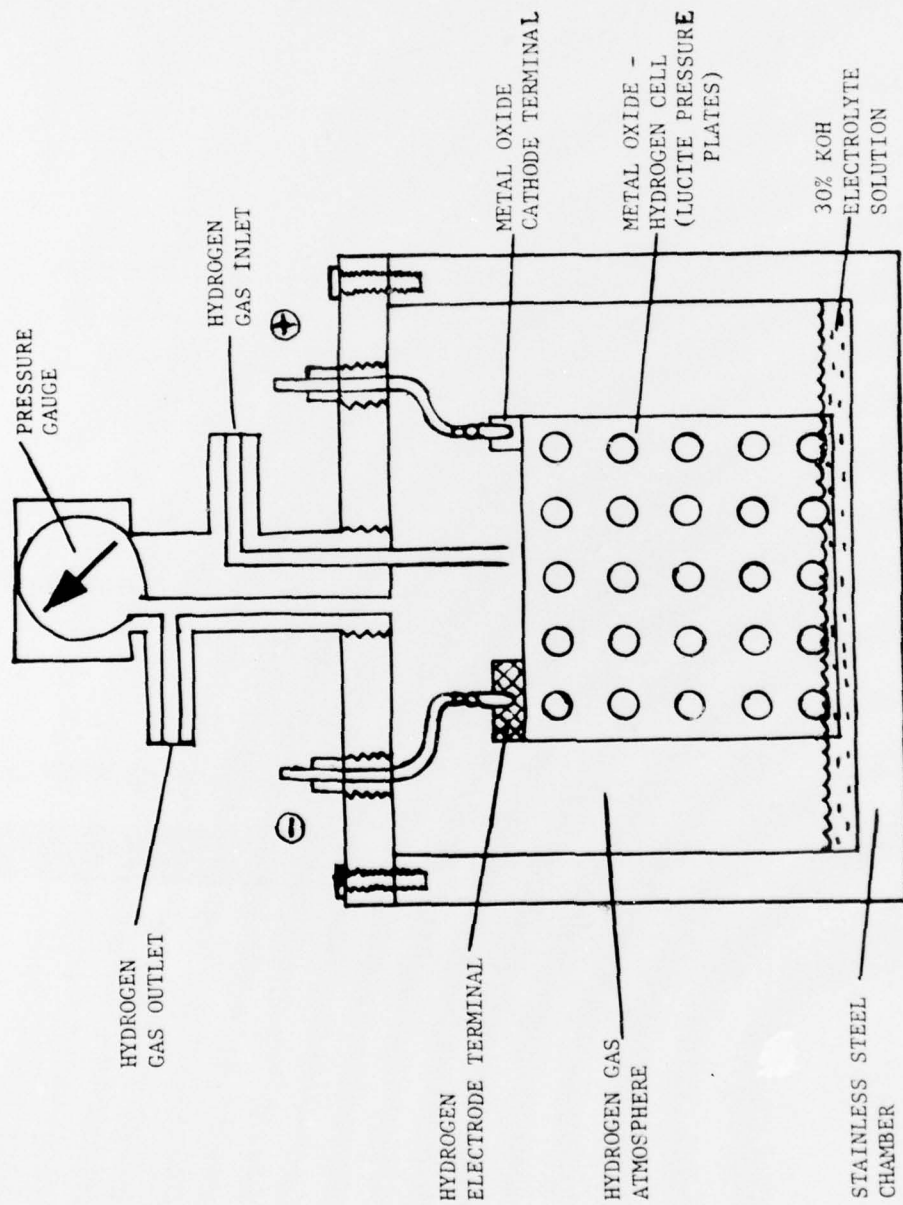


Figure 4. Experimental Metal Oxide-Hydrogen Test Cell Chamber



Prior to the charging and discharging of the electrode packs, the pressure vessels were vacuumed and purged with hydrogen several times in order to provide a pure hydrogen atmosphere to the inclosed systems. Cell voltages were recorded on Hewlett-Packard 7100B strip chart recorders. At the 2.2 maximum ampere rate, the corresponding current densities were 110 mA/cm<sup>2</sup> for the nickel oxide-hydrogen cells and 100 mA/cm<sup>2</sup> for the silver oxide-hydrogen cells. During cell charging, the charge time was adjusted to overcharge the cells by 27.5% (of nominal rated capacity) for both the nickel oxide and silver oxide-hydrogen cells.

## RESULTS AND DISCUSSION

Typical charge-discharge curves of both types of cells are shown in Figure 5. The charge curves of the silver oxide-hydrogen cells contain three voltage plateaus while those of the nickel oxide-hydrogen cells contain one voltage plateau. The computed average values of the charge voltages for the two metal-hydrogen cells were only about 0.1 volt difference. For example, at a charge current density of 37.5 mA/cm<sup>2</sup>, average potential of the NiO/H<sub>2</sub> cell was 1.44 V while that of the AgO/H<sub>2</sub> was 1.525 V (Table 1).

Table 1. Voltage-Time Plateaus for Charging NiO/H<sub>2</sub> and AgO/H<sub>2</sub> Cells.

NiO/H <sub>2</sub>			AgO/H <sub>2</sub>		
TIME (HR)	VOLTAGE (V)	VOLTAGE DIFFERENCE (V)	TIME (HR)	VOLTAGE (V)	VOLTAGE DIFFERENCE (V)
0.9	1.360 - 1.450	0.090	0.48	1.245 - 1.320	0.075
1.72	1.450		0.65	1.320 - 1.620	0.300
			0.15	1.620 - 1.770	0.150
Average Voltage = 1.440 V			Average Voltage = 1.525 V		

On discharge (Figure 5), the NiO/H<sub>2</sub> cell exhibited one voltage plateau while the AgO/H<sub>2</sub> cell had two plateaus. A more detailed evaluation of both types of the metal oxide-hydrogen cell are given in the following sections.

1. Nickel Oxide-Hydrogen Cells. Figure 6 shows the average cell voltages on charge and discharge, as well as percent charge/discharge efficiencies of the nickel oxide-hydrogen cells as a function of current density up to the 2.2 ampere rate. Up to the maximum current level of the test equipment (110 mA/cm<sup>2</sup>), the charge/discharge voltages appeared reversible. The charge/discharge efficiencies were greater than 70%, the



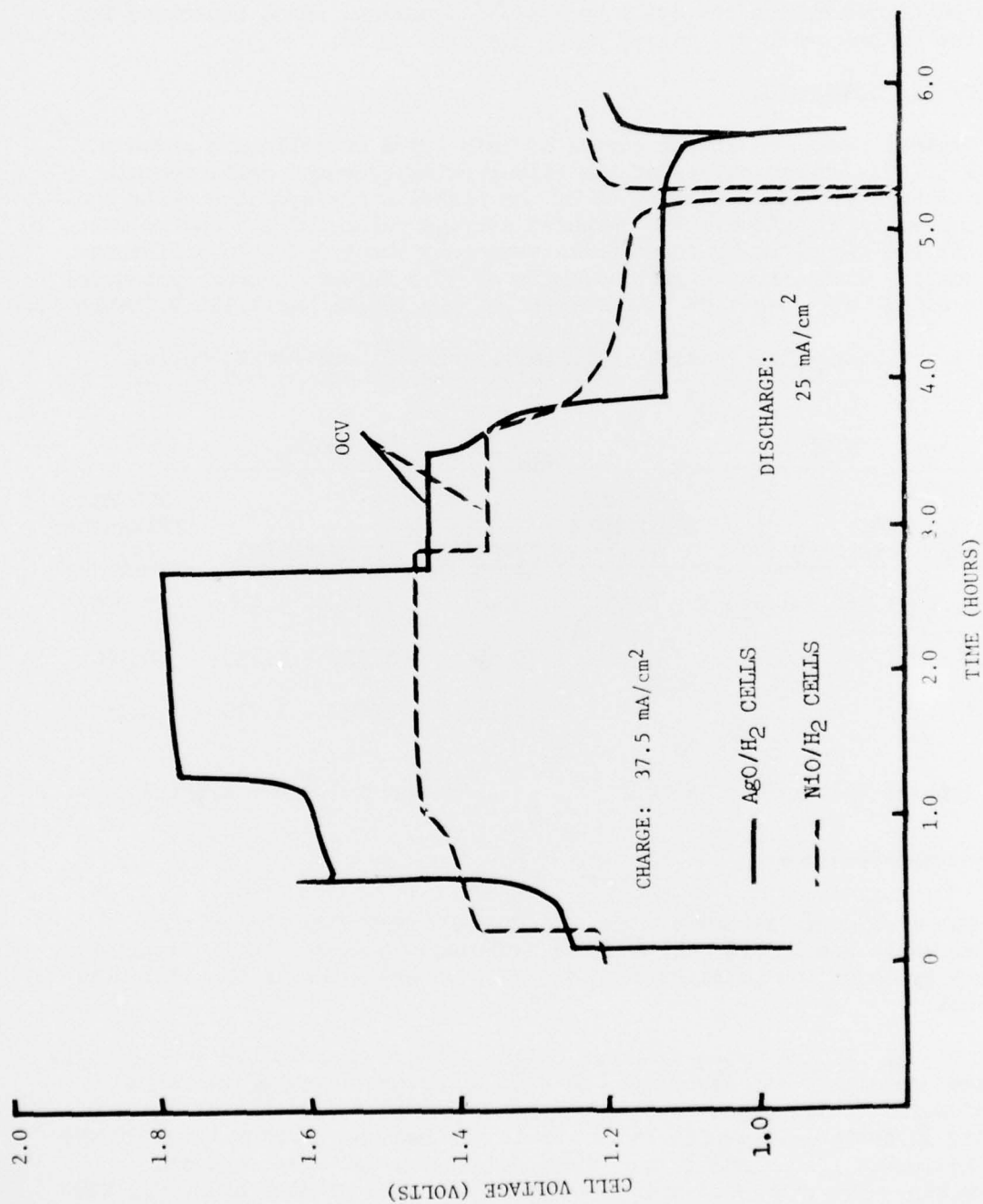


Figure 5. Charge/Discharge Curves of Nickel Oxide-Hydrogen and Silver Oxide-Hydrogen Cells

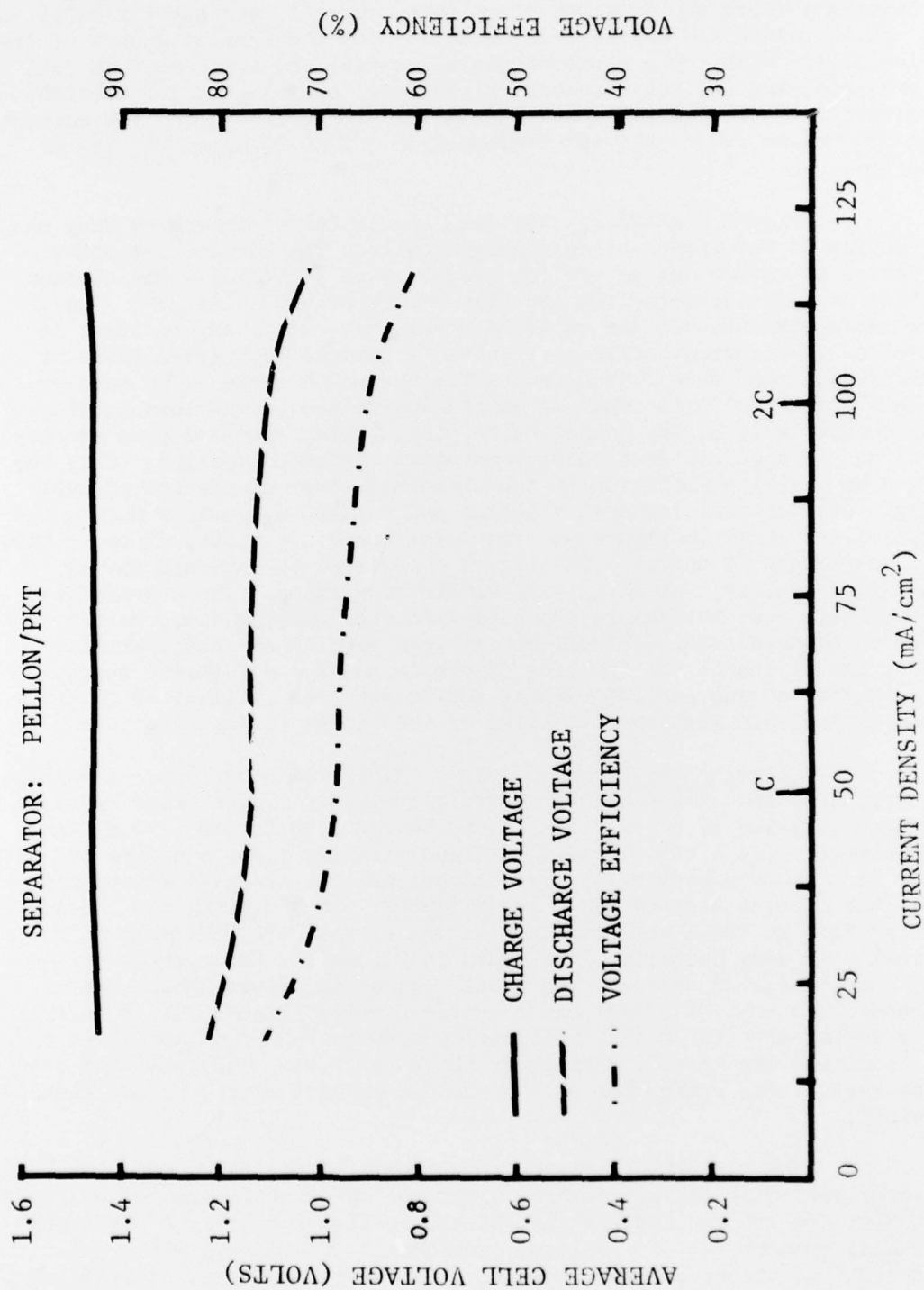


Figure 6. Voltage Characteristics vs Current Density for NiO/H<sub>2</sub> Cells

charge potential was stable at about 1.50 volts, and the discharge potential decreased from 1.18 volt at 25 mA/cm<sup>2</sup> to 1.08 volt at 110 mA/cm<sup>2</sup>. The major energy losses in charging nickel oxide-hydrogen cells are shown in Figure 7. The losses are expressed in terms of voltage, current, and overall efficiencies. These losses are mainly attributed to: (a) the limited amount of free KOH electrolyte within the sintered nickel matrix, (b) a non-uniform cell pack pressure, and (c) the resulting higher cell ohmic and concentration overpotentials. The overall losses are mainly reflected in the low current efficiency values, where the value drops from 55% at 25 mA/cm<sup>2</sup> to 35% at 110 mA/cm<sup>2</sup>.

Figure 8 shows how the cell electrical efficiencies vary on life cycling of the nickel oxide-hydrogen cells. The current densities were varied at random during cycling from 12.5 to 35 mA/cm<sup>2</sup> - the current densities used for constructing the figure were around 20 mA/cm<sup>2</sup>. The figure shows that the voltage efficiency remained relatively constant to 794 cycles. The current efficiency showed a gradual drop after which it decreased at a more accelerated rate after the 660th cycle. The accelerated loss in current efficiency is mainly attributed to the loss in electrical conductivity of the nickel oxide plaque which resulted from embrittlement and loss of sintered contact points on repeated cycling. This was verified by visual examination of the electrode after completion of cell cycling. Cell charge/discharge voltages and voltage efficiency during the 794 cycles are shown in Figure 9. The points used for construction of this figure are around 20 mA/cm<sup>2</sup>. The figure shows that the average charge voltage increases very slightly with continued cycling. The average discharge voltage does not change appreciably during cycling since only average voltages above 1.0 V/cell cutoff were used in the computations. However, the discharge voltage-time intervals above 1.0 V became successively shorter during cycling because active material utilization of the cathode dropped off with the breakdown of the nickel sinter-structure.

2. Silver Oxide-Hydrogen Cells. Figure 10 shows typical voltage characteristics and charge/discharge efficiencies of silver oxide-hydrogen cells as a function of current density up to the 1.46 C rate (110 mA/cm<sup>2</sup>). The discharge voltage curve (second plateau) is very flat, a desirable feature in high rate batteries. The charge plateaus are also reasonably flat in the current density range investigated. In addition, the charge/discharge voltage efficiency remained at values that are tolerable in practical secondary batteries. As shown in Figure 11, the current efficiency for the silver oxide-hydrogen cell sustained a loss, which was comparable with that of nickel oxide-hydrogen cells (Figure 7). Figure 11 shows a linear drop in Faradaic efficiency between 35 mA/cm<sup>2</sup> and 75 mA/cm<sup>2</sup>. Above 75 mA/cm<sup>2</sup> the current efficiency tends to increase somewhat and then decline again. The reason for this anomalous characteristic is not clearly understood.

The current efficiency in both the silver oxide and nickel oxide-hydrogen cells can possibly be increased by using separators of lower resistivity and interseparators that possess better electrolyte retention and wicking properties. In addition, employment of cathodes with reinforced sintered structures should improve the active material utilization on prolonged cycling and thereby stabilize the Faradaic efficiencies of the electrodes.

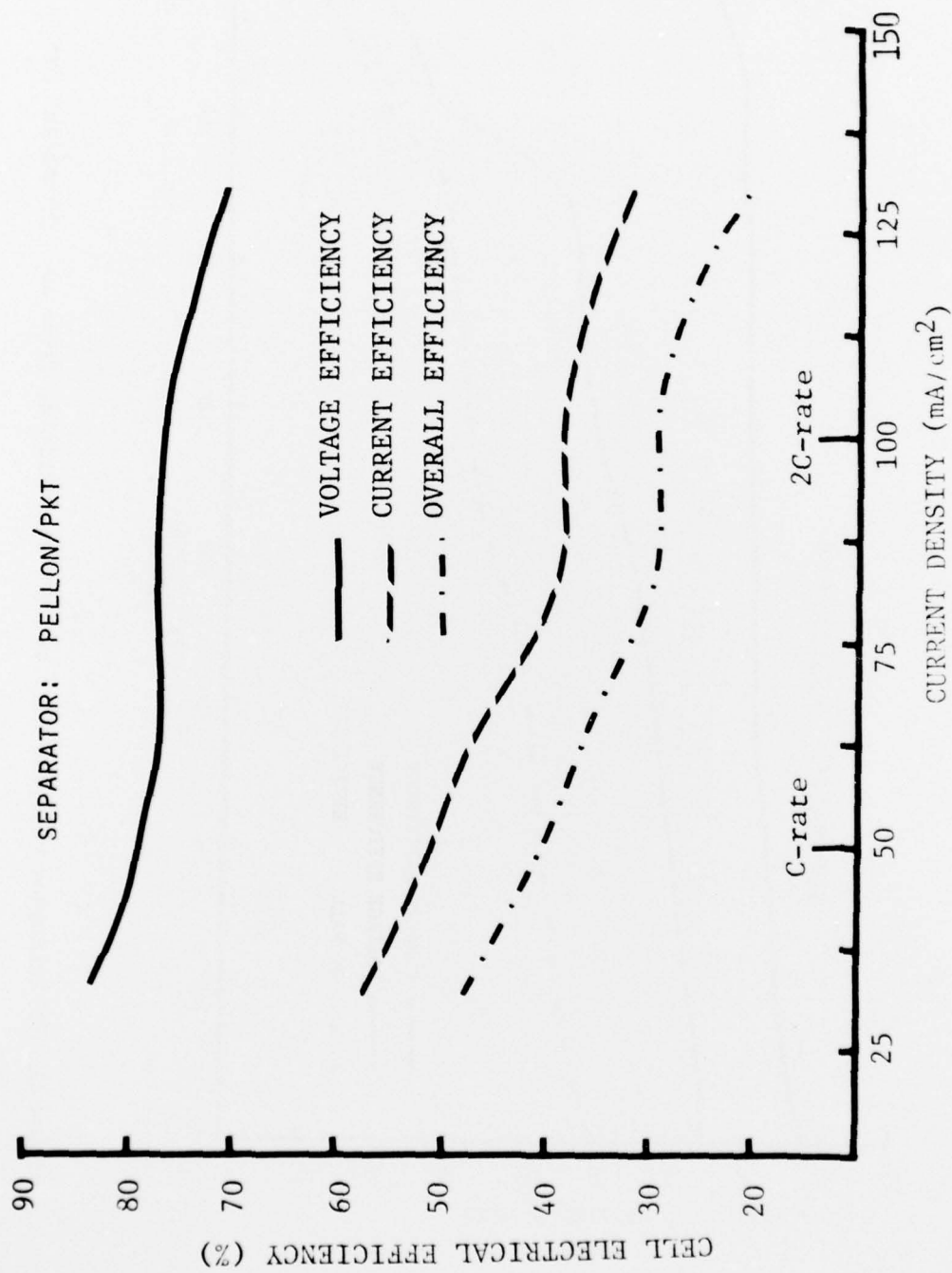


Figure 7. Efficiencies vs Current Density for NiO/H<sub>2</sub> Cells

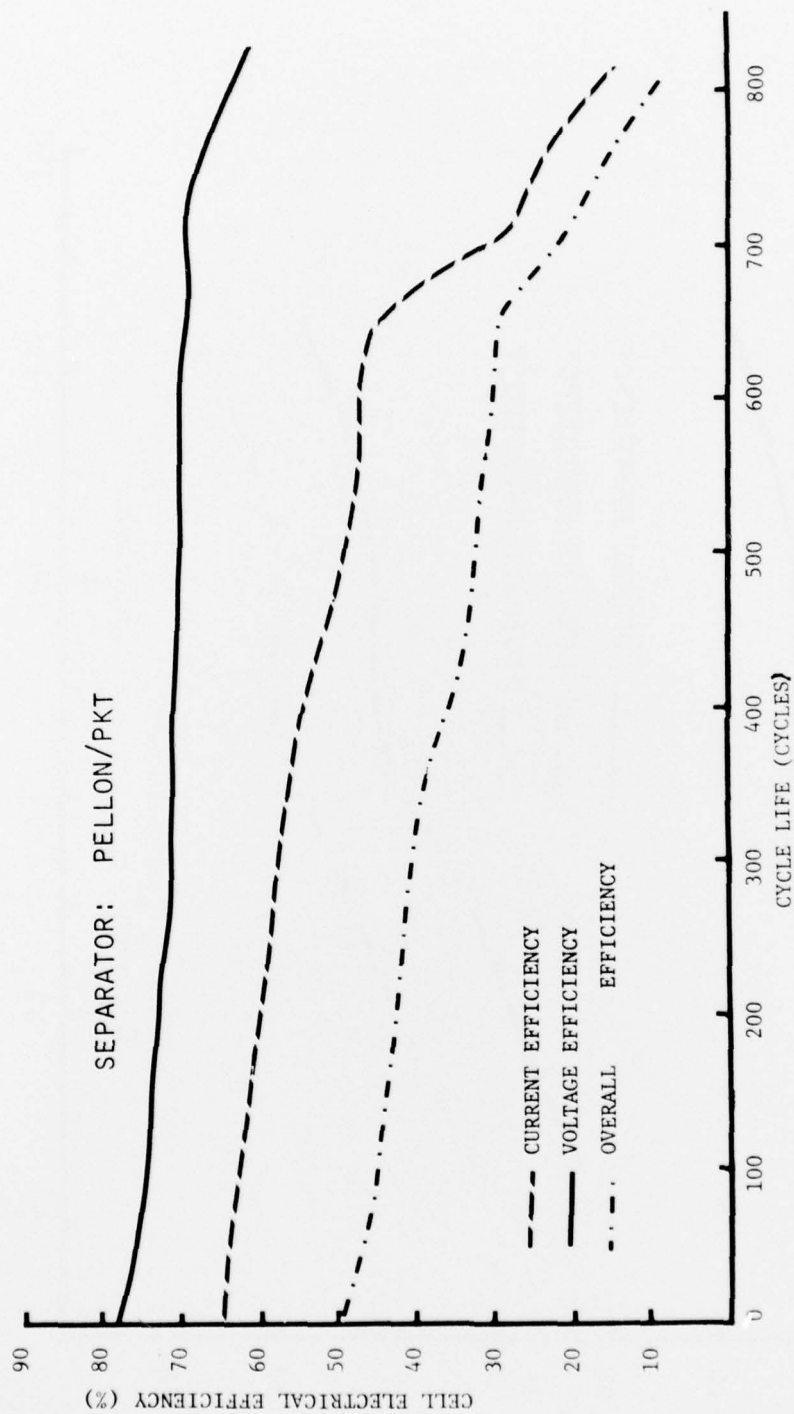


Figure 8. Efficiencies vs Cycle Life at Current Densities from ~ 20 mA/cm<sup>2</sup> for NiO/H<sub>2</sub> Cells



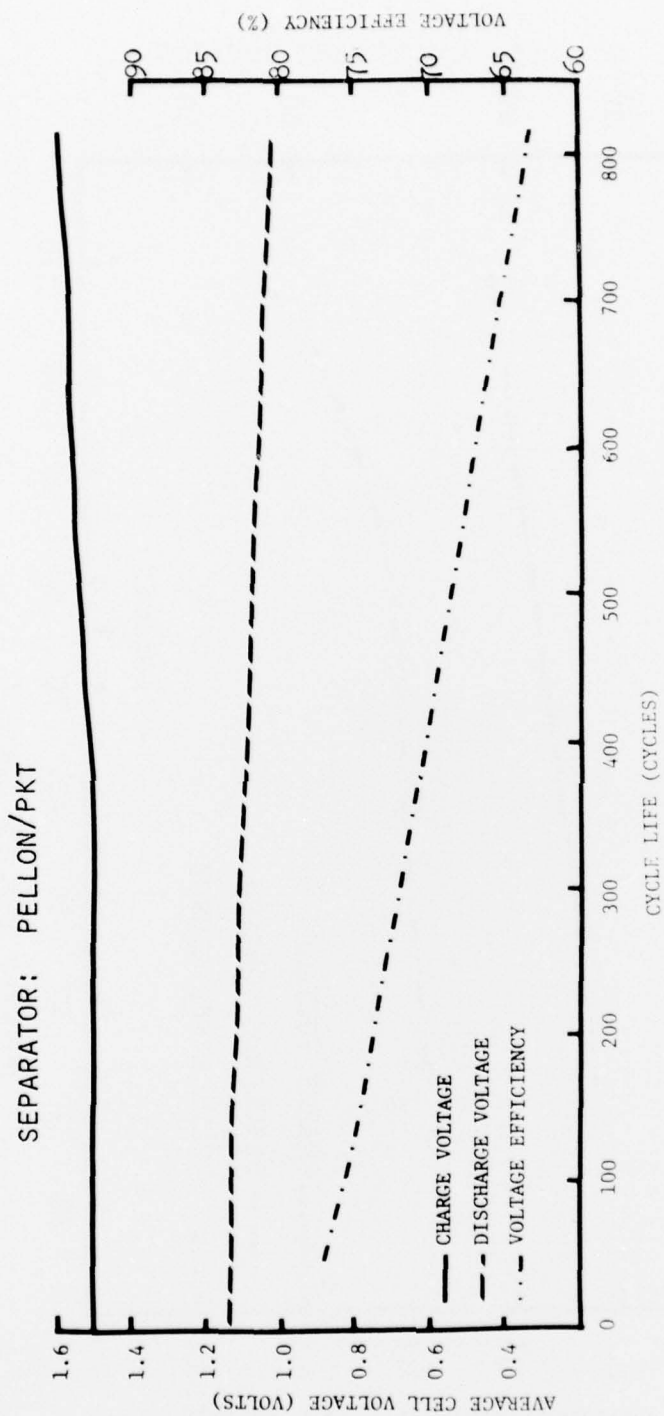


Figure 9. Voltage Characteristics vs Cycle Life for NiO/H<sub>2</sub> Cells



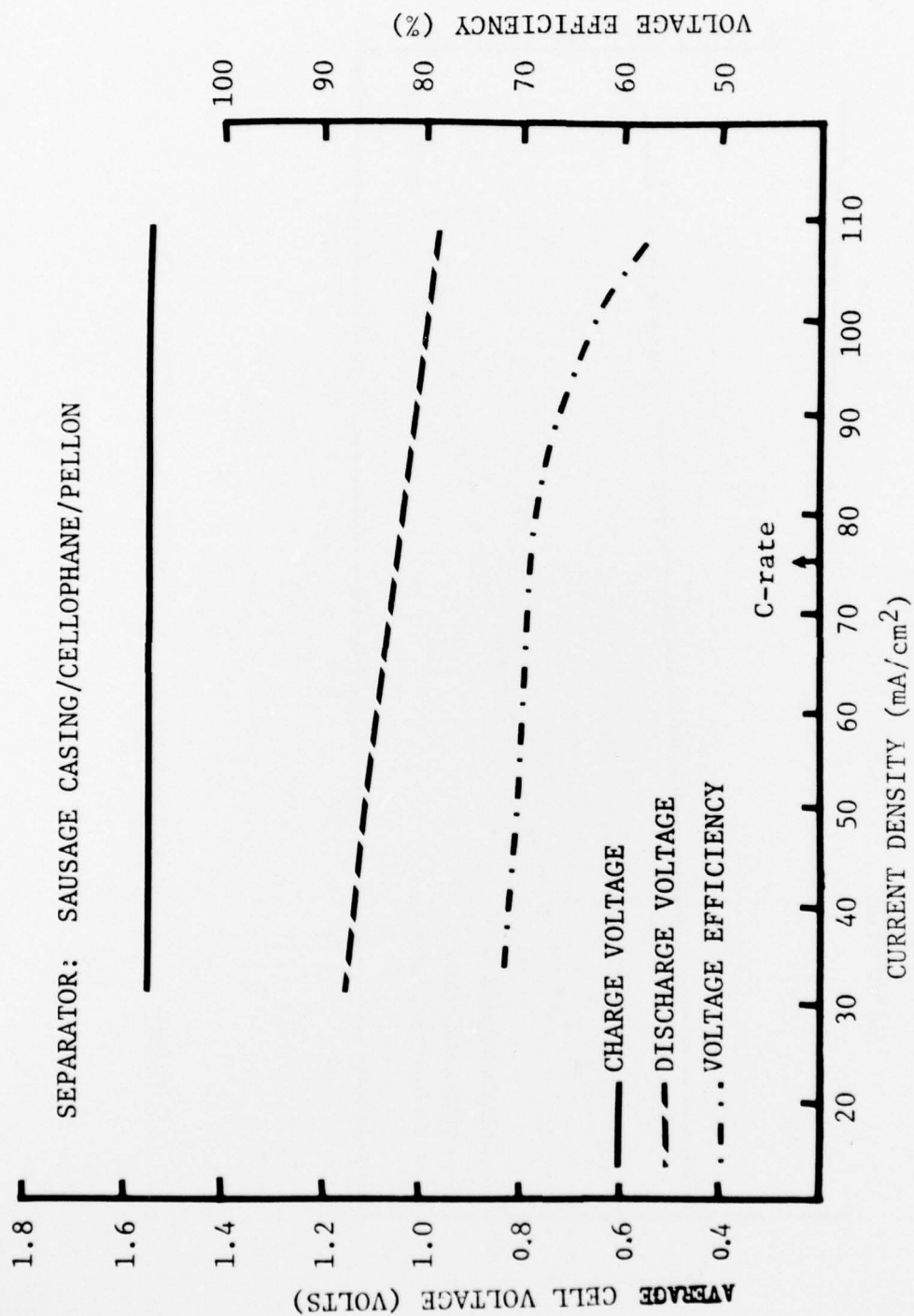


Figure 10. Voltage Characteristics vs Current Density for AgO/H<sub>2</sub> Cells

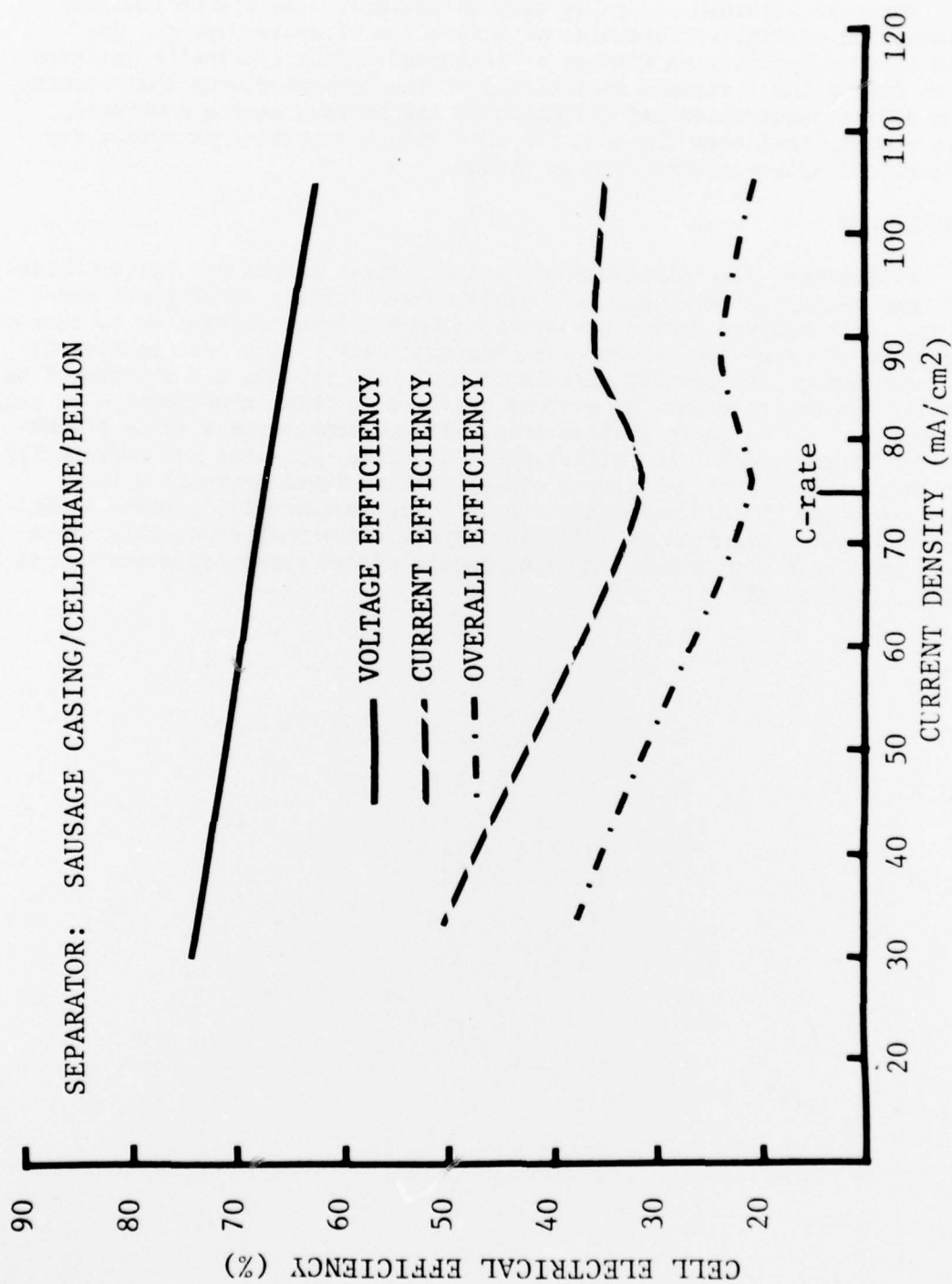


Figure 11. Efficiencies vs Current Density for AgO/H<sub>2</sub> Cells

A major shortcoming of the silver oxide-hydrogen system is its limited cycle life due to silver penetration of the separator wrap which consisted of 2 layers of sausage casing and cellophane sandwiched between two layers of Pellon, as shown in Figure 12. The figure shows that the cell attained 32 cycles without failure. The figure includes voltage and current efficiencies as a function of cycle number. The main drop in current and voltage efficiencies during cycling is believed to be due to the increased resistivity of the separator wrap that results from silver penetration and oxidation of the sausage casing membranes. This clearly indicates the need for more stable separator materials for a practical silver oxide-hydrogen system.

#### CONCLUSIONS

Preliminary investigations on nickel oxide-hydrogen and silver oxide-hydrogen cells indicate that both systems need further development and study. Both systems showed excellent voltage characteristics up to current densities of about  $110 \text{ mA/cm}^2$  - the maximum limit of the test equipment. The relatively poor current efficiencies of both systems are attributed to the limitations of separator systems employed in this investigation as well as poorly sintered cathode structures. The separators were state-of-the-art for nickel-cadmium and silver-zinc batteries, but were not necessarily optimal for metal oxide-hydrogen cells. Future tests on metal oxide-hydrogen cells containing separators of lower resistivity, greater stability, and better electrolyte retention appear warranted, especially since there have been many promising developments of new separator materials in battery technology.

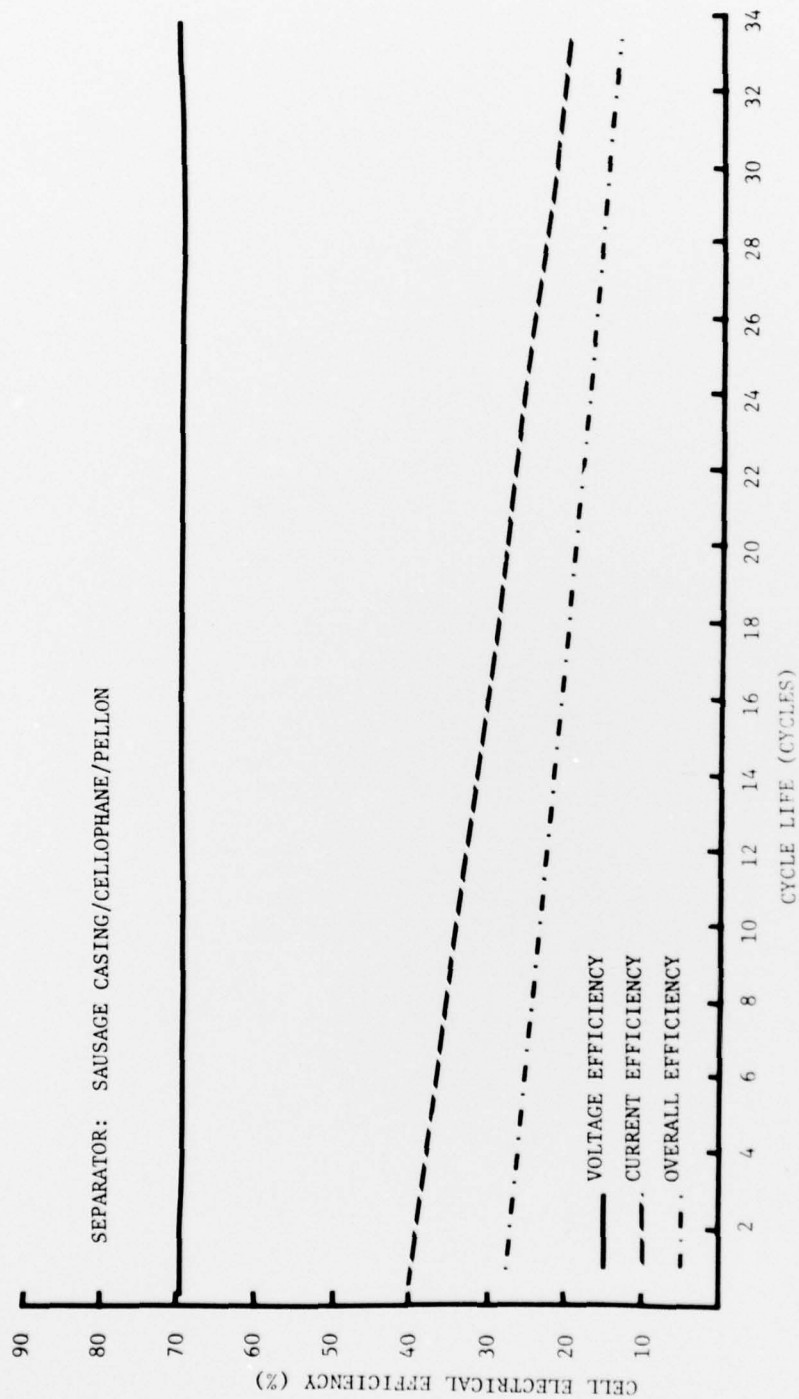


Figure 12. Efficiencies vs Cycle Life at a Current Density of 50 mA/cm<sup>2</sup> for AgO/H<sub>2</sub> Cells